Progress Report

August 2000

Contract Number A-36B

Data Analysis for a Better Understanding of the Weekday/Weekend Ozone and PM Differences

Prepared for

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Introduction

Atmospheric and Environmental Research, Inc. (AER) is providing consulting service to the Coordinating Research Council, Inc. (CRC) under CRC Contract Number A-36B for the project titled "Data Analysis for a Better Understanding of the Weekday/Weekend Ozone and PM Differences".

The project period is from 18 October 1999 to 18 September 2000.

Work Performed in May 2000 – August 2000

Characterization of Weekday/Weekend Differences in O_3 and PM

Our last progress report summarized the weekly behavior of ozone (O_3) in three cities, Atlanta, GA; Chicago, IL; and Philadelphia, PA; and PM_{10} in Chicago, IL. During this project period, we have downloaded PM data in Atlanta and Philadelphia and completed the analysis of the day-of-week behavior of PM, as summarized below.

Atlanta. Data from the only PM_{10} monitoring station in the Atlanta metropolitan area produced very jagged daily concentration profiles when plotted by the day of the week because of limited record length (one year). The 24-hour concentrations, grouped by the day of the week and averaged over the one-year record, were highest on Tuesdays (28 $\mu g\ m^{-3}$) and lowest on Sundays (24 $\mu g\ m^{-3}$). The difference was significant at the 10% level.

$PM_{2.5}$ data were available as 24-hour averages from 8 sites in 1999. Like O_3, 24-hour average $PM_{2.5}$ concentrations in Atlanta (Figure 1) were lowest on Mondays, followed by Sundays (18 to 19 $\mu g\ m^{-3}$). High $PM_{2.5}$ concentrations were observed late in the week, i.e., Thursdays, Saturdays, and Fridays (22 $\mu g\ m^{-3}$). The observed differences between the concentrations on Mondays and Wednesdays through Saturdays were significant at the 5% level. The differences between Sundays and Thursdays through Saturdays were significant at the 10% level. When weekdays and weekend days were grouped as two groups, no difference was observed in the difference of the mean values. However, the difference between the mean Tuesday-through-Saturday and Sunday-to-Monday concentrations was highly significant.

Chicago. Thirteen $PM_{2.5}$ sites were in operation during 1999, measuring 24-hour average concentrations on every third day. With about 15 data points for each day of the week, high $PM_{2.5}$ concentrations were observed on Saturdays, Fridays, and Wednesdays, and low concentrations were observed on Tuesdays, Thursdays, and Mondays. The high-low differences were significant at the 5% level at 12 sites and at the 10% level at the remaining site. On average, the mean $PM_{2.5}$ concentration on weekdays was lower than that on weekends by 3 $\mu g\ m^{-3}$. This difference was significant at the 10% level.

Philadelphia. PM_{10} data were available from two Philadelphia area sites from 1995 to 1998. The average concentration profiles (Figure 2) showed a marked PM increase between 5 a.m. and 8 a.m. on weekdays as compared to weekends. Throughout the day, PM concentrations were higher on weekdays than weekends. The 24-hour average concentrations of PM_{10} were highest on Wednesdays and Thursdays and lowest on Sundays. The differences between all pairs of weekday-weekend 24-hour average concentrations were significant at the 5% level.

$PM_{2.5}$ data were also available at one site for 9 months in 1999. No day-of-the-week trends could be observed from the diurnal concentration profiles. The 24-hour average concentrations were lowest on Thursdays and highest on Saturdays followed by Tuesdays. The differences between the high-low pairs were significant at the 10% level. However, there was no statistical difference between weekday concentrations and weekend concentrations as two groups.

Hypothesis Testing

Initial results of the hypothesis testing phase of project A-36B are presented next, including some correlations of VOC, NO_x, and CO with O_3 used to test the hypotheses put forth in the proposal.

Hypothesis 1. Increase in VOC/NO_x ratio during the weekend leads to increase in O_3 in a VOC-sensitive airshed.

We present the changes in the 24-hour average VOC/NO_x (ppbC/ppb) ratio in the table below for the three cities of interest. In Atlanta and Chicago, the differences between the weekday and weekend VOC/NO_x ratios were significant at the 5% level; whereas in Philadelphia, the difference was significant at the 10% level.

Increases in O_3 during weekends were observed at Chicago and Philadelphia, and Atlanta tended to have lower O_3 concentrations during the weekend. From the ratios in the table, it was expected that Chicago may be the most VOC-sensitive location, where NO_x reduction disbenefit may explain the weekend effect, i.e., the increase in weekend O_3 relative to weekdays. In Philadelphia, the VOC/NO_x ratios would not indicate VOC sensitivity. When we correlated the VOC/NO_x ratio to the maximum one-hour O_3 concentration, grouped by the day of the week, the strongest correlation was observed in Chicago, meaning O_3 concentrations increased almost linearly with increases in the VOC/NO_x ratio. The correlation was expectedly poor in Atlanta, where weekend O_3 increases were not observed. The weak correlation in Philadelphia seemed to indicate that (1) the weekend effect may be due in part to reduced local O_3 titration by NO_x and (2) the formation of O_3 may occur in part in upwind locations that are VOC-sensitive.

	Atlanta, GA	Chicago, IL	Philadelphia, PA
weekday VOC/NO_x ratio	5.6 – 6.6	2.3 – 2.5	9.4 – 10.5
weekend VOC/NO_x ratio	7.9 – 8.4	3.1 – 3.5	11.0 – 14.1
correlation coefficient between O_3 and ratio	0.04	0.98	0.67
R^2 value	0.00	0.96	0.45

Hypothesis 2. Increased traffic on Friday and Saturday evenings leads to increased carry-over of precursors and increased O_3 formation potential on the weekends.

To test this hypothesis, we compared the predawn concentrations of precursors, including NO_x and CO (the latter as a tracer for VOC emissions from traffic). In Atlanta, Chicago and Philadelphia, NO_x before dawn on weekdays was higher by 5 ppb on average than weekends; while CO was higher on weekends by 160 ppb, 60 ppb and 160 ppb in Atlanta, Chicago, and Philadelphia, respectively. The differences in the precursor concentrations in the predawn hours were statistically significant at the 5% level. These observations were consistent with increased passenger car traffic and reduced truck traffic on Friday and Saturday nights in Atlanta, Chicago, and Philadelphia.

The correlations between predawn NO_x concentrations and O_3 in Chicago and Philadelphia were consistent with the O_3 vs. VOC/NO_x ratio correlations, albeit weaker than the latter. In Atlanta, there was some positive correlation between O_3 and the NO_x concentration before the morning rush hour, despite the lack of correlation with the VOC/NO_x ratio. Production of O_3 in Atlanta may be sensitive to NO_x carry-over, as discussed later.

The O_3-CO correlation was non-existent in Atlanta. In Chicago, a weak positive correlation was also consistent with the observations from the O_3-VOC/NO_x correlation. The relatively strong positive correlation between O_3 and predawn concentrations of CO provided some evidence that the availability of VOC precursors could be important to the formation of O_3 in Philadelphia.

	Atlanta, GA	Chicago, IL	Philadelphia, PA
weekday predawn NO_x	28 – 38 ppb	38 – 51 ppb	36 – 43 ppb
weekend predawn NO_x	26 – 33 ppb	37 – 46 ppb	29 – 39 ppb
correlation coefficient between O_3 and predawn NO_x	0.70	- 0.58	-0.57
R^2 value	0.50	0.34	0.32
weekday predawn CO	0.76 – 0.83 ppm	0.69 – 0.73 ppm	0.72 – 0.75 ppm
weekend predawn CO	0.90 – 0.99 ppm	0.75 – 0.78 ppm	0.87 – 0.91 ppm
correlation coefficient between O_3 and predawn CO	0.11	0.77	0.92
R^2 value	0.01	0.59	0.85

Hypothesis 2a. Carry-over of precursors from one day to the next as the driving force for the weekly cycle of ozone.

At sites that seemed to be sensitive to the predawn concentrations of precursors, there is a distinct possibility that it is not only the night-time emissions, but also the carry-over of precursors that drive the weekly behavior of O_3 concentrations. We investigated the correlations of O_3 vs. previous day's NO_x, NO_y, CO, and VOC, focusing on NO_x and NO_y for Atlanta and VOC and CO for Chicago and Philadelphia, based on the predawn concentration correlations. The results are reported in the following table.

correlation coefficient between O_3 and 24-hour concentration from the previous day	Atlanta, GA	Chicago, IL	Philadelphia, PA
NO_x (R^2)	0.75 (0.56)	-0.22 (0.05)	-0.40 (0.16)
NO_y (R^2)	0.87 (0.76)	0.06 (0.00)	0.41 (0.17)
CO (R^2)	0.81 (0.65)	-0.09 (0.01)	-0.07 (0.00)
VOC (R^2)	0.28 (0.08)	0.56 (0.31)	0.31 (0.09)

The daily maximum O_3 in Atlanta correlated well with previous day's 24-hour average NO_x, NO_y and CO concentrations. In fact, the R^2 values were much higher than the corresponding relationship with the NO_x, NO_y and CO concentrations from the same day. The positive correlation coefficients indicated that NO_x and NO_y from previous days fueled O_3 production, rather than scavenged it. The VOC correlation was much weaker (for both same day and with a 1-day lag). Therefore, the weekly O_3 behavior in Atlanta, including minimum O_3 concentrations on Mondays, may be driven in part by the amount of NO_x and NO_y carried over from previous day(s). On the other hand, it is not sensitive to VOC carry-over as expected from the VOC/NO_x ratio. In Chicago and Philadelphia, carry-over of precursors seemed to play a small role; weak or negligible correlations were observed with O_3 concentrations. (For example, in Chicago, the correlation coefficient between O_3 and the same day's 24-hour average NO_x was -0.97, vs. a mere -0.22 with NO_x concentration of the previous day.)

Hypothesis 6. Reduction in fine PM emissions during weekends results in increased photochemical activity and O_3 production during weekends.

There are two components to this hypothesis. First, we attempted to identify if any changes in photochemical activity could be detected in solar radiation as a function of the day of the week. At all three sites, solar radiation tended to increase during weekends. Statistically significant increases were observed in Philadelphia (5%) and Atlanta (10%), but not in Chicago. Correlations results of solar radiation with O_3 are shown in the next table. Increases in solar radiation were associated with increases in O_3, but the correlations were weak, especially in Atlanta.

Second, we tested to see if the changes in solar radiation are related to changes in particle concentrations. $PM_{2.5}$ is of interest because fine particles are efficient light scatterers. In Atlanta, no significant correlation was expected because of the lack of O_3 increase over the weekend. In Chicago, both O_3 and $PM_{2.5}$ increased during weekends (although there was no significant correlation between O_3 and $PM_{2.5}$). The positive PM-radiation correlation results did not support the hypothesis that the observed increase in weekend solar radiation was caused by reductions in $PM_{2.5}$ emissions. The weekly trend of $PM_{2.5}$ was not well-defined in Philadelphia, possibly because of limited data (only 1 site for 9 months). Therefore, while the weak positive correlation with radiation seemed to be inconsistent with the hypothesis that a decrease in $PM_{2.5}$ was related to an increase in photochemistry, the hypothesis cannot be considered disproved at this site.

	Atlanta, GA	Chicago, IL	Philadelphia, PA
correlation coefficient between O_3 and 24-hour average solar radiation (R^2)	0.23 (0.06)	0.63 (0.39)	0.56 (0.31)
correlation coefficient between 24-hour average solar radiation and $PM_{2.5}$ concentration (R^2)	0.04 (0.0)	0.80 (0.63)	0.35 (0.13)

Work to be Performed

In the next weeks, we plan to complete the hypotheses testing phase of the project. Key analyses to be performed include the weekday-weekend differences in the spatial distribution of pollutants (activity patterns) and, where sufficient data exist, changes in VOC/PM composition that might reflect changes in emission sources. In addition, we plan to download O_3 data from a pre-reformulated gasoline period from the AIRS database to assess any changes in the day-of-the-week behavior over the long term.

A draft final report will be submitted in September to CRC.

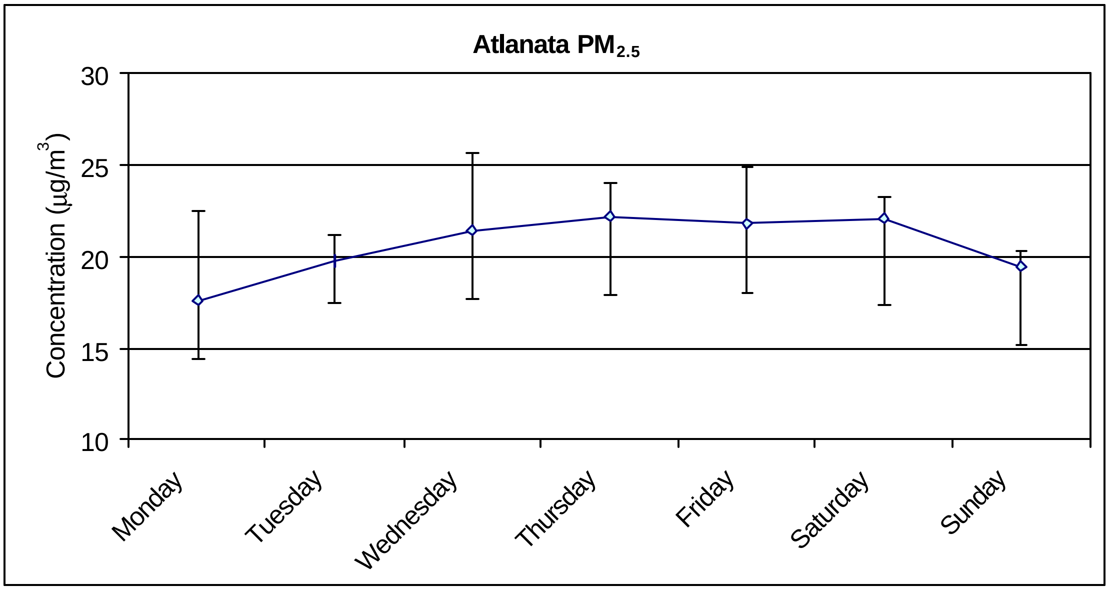

Figure 1. Mean 24-hour average concentration of $PM_{2.5}$ in Atlanta, GA, grouped by day of the week. (Symbols represent the spatial average concentration of 8 sites, grouped by day of the week; error bars indicate ranges of values at individual sites)

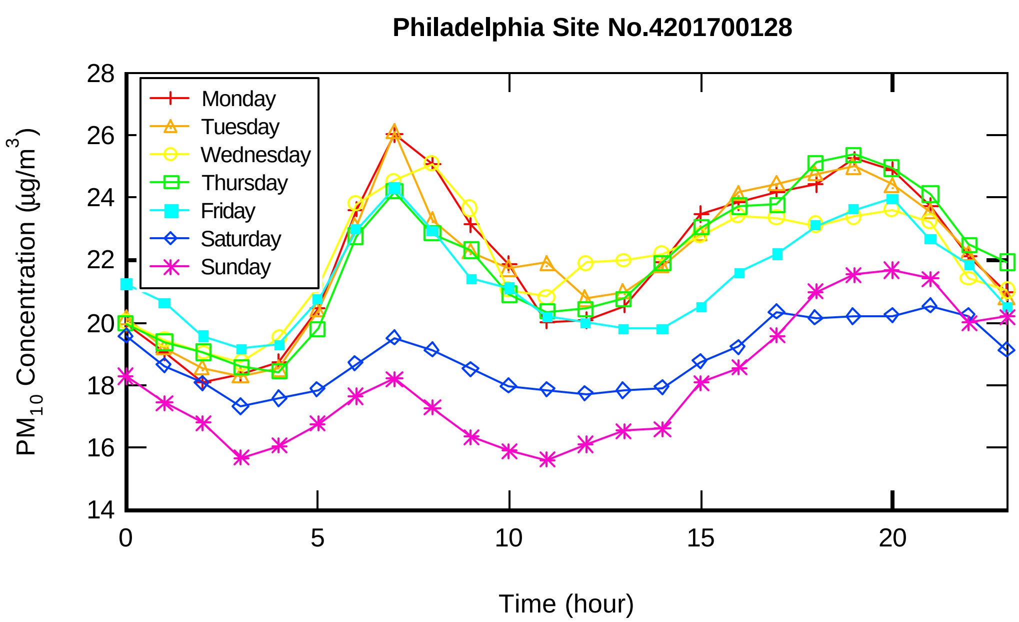

Figure 2. Averaged PM_{10} diurnal profiles at Site No. 4201700128 in Philadelphia, PA.